



Rational design of MoS₂@COF hybrid composites promoting C-C coupling for photocatalytic CO₂ reduction to ethane

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ARTICLE INFO

Keywords:

COF
MoS₂
Interfacial charge transfer
Photocatalytic CO₂ reduction
Ethane

ABSTRACT

Photocatalytic CO₂ reduction into high-value C₂₊ products such as ethane is quite exciting but challenging due to multielectron steps involved and sluggish C-C coupling kinetics. Herein, a well-designed MoS₂@COF hybrid composite is prepared for efficient and selective CO₂ photoreduction to C₂H₆. In-depth experimental and theoretical studies reveal that the interfacial electric field built in the heterojunction accelerates the photogenerated electrons transfer from MoS₂ to COF under light irradiation, greatly facilitating charge separation and transfer and thus enhancing the activity and C₂H₆ selectivity for CO₂ photoreduction. The optimized MoS₂@COF-15 achieves C₂H₆ production rate up to 56.2 μmol·g⁻¹·h⁻¹ with 83.8% of selectivity, which is about 8.6 and 31.2 times higher than that of pristine MoS₂ and COF under identical conditions. The in-situ DRIFTS and DFT calculations indicate that the structure of MoS₂@COF composite can promote the adsorption of *CO and the formation of *COCO, facilitating C-C coupling to convert into C₂H₆ product.

1. Introduction

The solar-driven carbon dioxide (CO₂) photoreduction into valuable hydrocarbons has been regarded as one of the most attractive ways to alleviate the greenhouse effect and energy shortages [1,2]. However, the inertness of liner CO₂ molecules and multiple proton-coupled electrons transfer steps pose great challenges related to the reaction activity and product selectivity [3]. Among all the possible products of CO₂ reduction, C₂₊ products such as ethane (C₂H₆) are more desirable ones because of higher energy density and economic values [4]. Nevertheless, most examples of photocatalytic CO₂ reduction reported currently mainly produced C₁ products (e.g., CO, CH₄, and HCOOH, etc.); in contrast, preferred high-value C₂₊ products were rarely achieved due to multielectron steps and sluggish kinetics for C-C coupling formation [5–7]. In particular, the conversion of CO₂ to C₂H₆ is more complex, involving 14-electron reaction process and the formation of many intermediates, which has a high activation energy barrier, resulting in lower efficiency and product selectivity [8–11]. Although considerable research efforts have been devoted to improving CO₂ reduction kinetics and tailoring product distribution, the photoreduction efficiency and product selectivity are still far from satisfactory. Therefore, it is imperative to explore effective photocatalysts to simultaneously improve the

efficiency and selectivity of photocatalytic CO₂ reduction to C₂₊ products, and a detailed understanding of the reaction mechanism also needs to be further clarified.

In recent years, covalent organic frameworks (COFs) have shown great potential in photocatalysis since the unique π -stacked structure endows them with defined pathways for charge carrier transfer or high photoconductivity [12,13]. Moreover, intrinsic characteristics of high surface area, tunable porosity and structural designability have also enabled COFs to show superior potential for CO₂ adsorption, diffusion, and activation [14]. Benefiting from these advantages, various COFs have been developed as photocatalysts for photocatalytic CO₂ reduction thus far [15–22]. It is worth mentioning that some COFs under visible light irradiation have been proven to be superior concerning traditional amorphous polymers and inorganic semiconductors. However, an undeniable fact is that the photocatalytic activity can hardly be further improved only by tuning their structures and band gaps because of the high recombination rate of photogenerated electron-hole pairs in single-component COFs [23,24]. Thus, how maximizing the photocatalytic activity of COFs still faces enormous challenges.

Recent studies demonstrated that integrating semiconductors with proper band positions into COFs to construct inorganic-organic hybrid composites is an effective solution to enhance photogenerated charge

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separation efficiency [25,26]. Various hybridization of COFs with other functional materials, including transition metal sulfides (e.g., CdS and FeS₂) [27–29], metal oxides (e.g., TiO₂, Bi₂WO₆, and α -Fe₂O₃) [30–32], metal-organic frameworks (MOFs) [33–36], and graphitic carbon nitride (g-C₃N₄) [37–39], have been developed and successfully applied for photocatalysis in the past decades. More importantly, the multi-component interfaces can modulate the electronic structures of photocatalysts and facilitate charge transfer and separation through the interfacial electric field, which results in a high electron density at catalytic sites, thereby presenting a superior performance in photocatalytic reactions [40,41]. Despite that, the key factors influencing catalytic efficiency are largely unknown in hybrid composites. Thus, it is still highly desirable to rationally construct COFs-based multicomponent composites with high activity for CO₂ photoreduction and uncover the photocatalytic mechanism.

Herein, we reported the hybridization of COFs with amino-modified molybdenum sulfide (MoS₂) to construct covalently integrated MoS₂@COF hybrid composites, in which the anthraquinone-based covalent organic framework was chosen to construct the heterostructure. The experimental and theoretical calculation results indicated that there was strong electron interaction between MoS₂ and COF to facilitate the separation and transfer of interfacial charge, such that it consequently contributed to the superior photocatalytic CO₂ reduction activity under visible light irradiation. Photocatalytic results demonstrated that the MoS₂@COF composites could accelerate multielectron reduction to produce C₂₊ hydrocarbons, especially C₂H₆, with high selectivity. With the resulting a series of MoS₂@COF composites, the highest C₂H₆ production rate under visible light reached up to 56.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which was 8.6 and 31.2 times that of pure MoS₂ and COF, respectively. The possible photocatalytic reaction mechanisms of CO₂ reduction were proposed on the basis of the in-situ spectra. This work highlights the interfacial engineering of the MoS₂@COF hybrid composites, which provides an impressive strategy to facilitate CO₂ conversion to C₂₊ hydrocarbons.

2. Experimental section

2.1. Materials

1,3,5-Triformylphloroglucinol (Tp, 97%) was obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. 2,6-Diaminoanthraquinone (DAAQ, 97%) was purchased from Shanghai Bide Pharmatech Co., Ltd. Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate ([Ru(bpy)₃]Cl₂·6H₂O) was purchased from Shanghai Haohong Pharmatech Technology Co., Ltd. Sodium molybdate (Na₂MoO₄·2H₂O, 99%) was purchased from Energy Chemical Co., Ltd. Extra pure mesitylene was purchased from J&K Scientific Co., Ltd. Ethylenediamine anhydrous (EDA, 99.5%), triethanolamine (TEOA, 99.5%), thiourea (CH₄N₂S, 99%), glacial acetic acid (CH₃COOH, 99.5%) and other common solvents were provided from local chemical suppliers. All the reagents are analytical grade and used without further purification prior to use.

2.2. Preparation of photocatalysts

2.2.1. Preparation of MoS₂ nanoflowers

The MoS₂ nanoflowers were synthesized through the traditional hydrothermal approach according to previous literatures with a slight modification [42]. Typically, 30 mL of EDA was slowly injected into 30 mL deionized water and continuously stirred for 0.5 h. Afterwards, 0.484 g of Na₂MoO₄·2H₂O and 0.762 g of thiourea were dissolved into the solution, which was further stirred for 15 min at room temperature and then transferred into a Teflon-lined stainless steel autoclave, heated at 200 °C for 24 h, and then air-cooled to room temperature. After the hydrothermal treatment completed, the obtained precipitate was filtered and sequentially washed with deionized water and ethanol for

several times, respectively, and dried at 60 °C for overnight under vacuum, finally yielding the amino-functional MoS₂ nanoflowers.

2.2.2. Synthesis of MoS₂@COFs hybrid composites

The MoS₂@COFs hybrid composites was obtained through two steps as follows. Firstly, 50 mg amino-functional MoS₂ and 50 mg 1,3,5-triformylphloroglucinol (TFP) were added to 20 mL DMF and then dispersed ultrasonically for 0.5 h. Subsequently, 0.2 mL 6 M CH₃COOH aqueous solution was added into the above solution stirred for 12 h at 50 °C. The obtained black solid was washed twice with acetone and dried at 60 °C for overnight under vacuum oven, referred to as MoS₂(CHO). Second, the obtained MoS₂(CHO) (5, 10, 15 and 20 mg), Tp (60 mg), DAAQ (102 mg), and DMAc/mesitylene (3/1 v/v, 3.6 mL) were added into a Schleck-flask (15 mL). After the slurry was sonicated for 30 min at room temperature, 6 M acetic acid (0.2 mL) was added into the mixture. Then, the Schleck-flask was degassed by three freeze-pump-thaw cycles, sealed off under vacuum, and heated at 120 °C for 3 days. After completion, the resulting red precipitate was collected by filtration and washed successively with *N,N*-dimethyl formamide and acetone for several times, and then dried at 60 °C under vacuum for 24 h to obtain red power, referred as the MoS₂@COF-*n* (*n* represents the amount of MoS₂(CHO) added). In addition, for comparison, the pure COF was prepared by the same procedure except for without the MoS₂(CHO).

2.3. Photocatalytic CO₂ reduction

The photoreduction CO₂ experiments were performed in a custom reaction reactor at ambient temperature and atmospheric pressure. A 300 W xenon lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd.) with a 420 nm-cut filter to cut off UV light (420–780 nm) was used as light source, which was positioned 10 cm away from the reactor. The focused intensity on the flask was ca. 209 mW/cm². In a typical process, photocatalyst (1.0 mg) and [Ru(bpy)₃]Cl₂·6 H₂O (5.0 mg) were dispersed into a mixed solution of acetonitrile (3.0 mL), deionized water (1.0 mL) and triethanolamine (1.0 mL), and the mixture was then ultrasonic for 10 min to form a homogeneous suspension solution. Prior to irradiation, the reaction system was filled with high-purity CO₂ (99.999%) for 5 min, repeated several times to exclude residual air in the reactor. Subsequently, the reactor was sealed and the light was turned on circulating cold water bath system, and the reaction system was maintained at 25 °C during photocatalytic reactions. The products of the CO₂ photocatalytic reduction were analyzed by gas chromatography equipped with thermal-conductive detector (TCD) and flame-ionization detector (FID) (GC9790II plus, Fuli Analytical Instrument Co., Ltd.). Isotope-labeled experiments were conducted with ¹³CO₂ instead of ¹²CO₂ and D₂O instead of H₂O under the same condition and the obtained gaseous products were analyzed by a GC-MS.

3. Results and discussion

3.1. Material synthesis and characterizations

The MoS₂@COF heterostructures were constructed via a facile in-situ synthetic process as illustrated in Fig. 1a. Briefly, MoS₂ was first synthesized using ethylenediamine as solvent through the previously reported solvothermal method with slight modification [42]. The NH₂ groups in as-synthesized MoS₂ can direct the sequent formation of COF through chemical reactions [33]. Fourier transformed infrared (FT-IR) spectroscopy shows a typical NH₂ stretching band at 3100–3300 cm⁻¹, indicating that NH₂ groups are successfully grafted on the surface (Fig. S1). Powder X-ray diffraction (PXRD) pattern of the aforementioned MoS₂ exhibit broad peaks at 17° and 33°, which are attributed to the (002) and (100) planes of hexagonal MoS₂ phase (Fig. S2) [43–45]. Then, the resulting MoS₂@COF composites were synthesized by introducing a certain amount of MoS₂(CHO), the surface functionalization of MoS₂ with 1,3,5-triformylphloroglucinol (Tp), into the reaction system

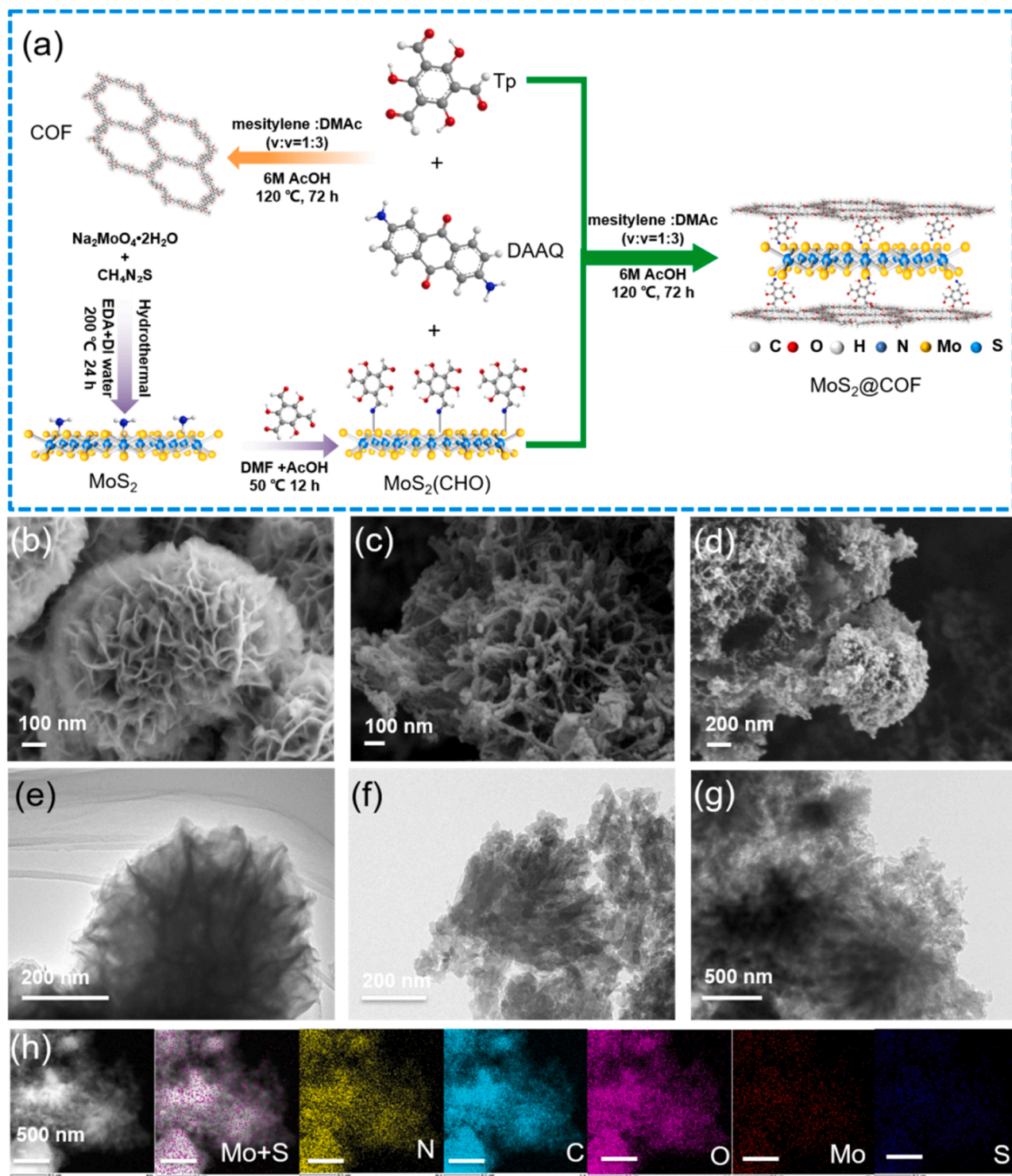


Fig. 1. (a) Schematic illustration of the synthesis of MoS₂@COF composites. SEM images of (b) MoS₂, (c) COF and (d) MoS₂@COF-15. TEM images of (e) MoS₂, (f) COF and (g) MoS₂@COF-15. (h) EDX elemental mapping of MoS₂@COF-15.

of constructing COF assembled from Tp and 2,6-diaminoanthraquinone (DAAQ) in *N,N*-dimethylformamide (DMF) by an acid-catalyzed condensation reaction. The same protocol was employed to synthesize a series of MoS₂@COF composites by adding different amounts of MoS₂, namely MoS₂@COF-5, MoS₂@COF-10, MoS₂@COF-15, MoS₂@COF-20 according to the amounts added of MoS₂, to maximize the reactivity.

The morphologies of as-synthesized MoS₂, COF and representative MoS₂@COF-15 composite were observed by scanning electron microscopy (SEM) and transmission electron microscope (TEM). Pristine MoS₂

presents a hierarchical flower-like morphology formed by self-assembly interweaving sheets with a diameter of approximately 500 nm (Fig. 1b, e), whilst COF shows a fibrous and flexuous morphology (Fig. 1c, f). The obtained MoS₂@COF-15 composite displays a similar morphology to COF (Fig. 1d, g). The TEM image of MoS₂@COF-15 further demonstrates that the flower-like MoS₂ is compactly wrapped in a thick layer of fibrous COF. The EDX elemental mapping results confirm the uniform distribution of C, N, O, Mo and S elements throughout the entire framework (Fig. 1h). SEM and TEM analyses verify the successful

preparation of the core-shell $\text{MoS}_2@\text{COF}$.

N_2 adsorption-desorption experiments at 77 K were conducted for MoS_2 , COF and $\text{MoS}_2@\text{COF-15}$ to assess their permanent porosity as presented in Fig. 2a. Both the isotherms of COF and $\text{MoS}_2@\text{COF-15}$ composite exhibit the reversible type I isotherms with H3 hysteresis loop, while the MoS_2 exhibits type IV isotherm, which is assigned to the stacking holes caused by aggregating particles. The Brunauer-Emmett-Teller (BET) surface area of $\text{MoS}_2@\text{COF-15}$ was calculated to be $731.3 \text{ m}^2\text{g}^{-1}$, which is lower than that of pristine COF ($945.4 \text{ m}^2\text{g}^{-1}$) (Table S1). Furthermore, the pore size distribution curves show that their pore width is centered at relatively narrow distributions of about 1.7 nm (Fig. S3). However, the pure MoS_2 almost has no pore channels with surface area of only $12.0 \text{ m}^2\text{g}^{-1}$. These results suggest that the integration of MoS_2 in the COF has no significant influence on the morphology and porosity, further reflecting the formation of core-shell structure. The XRD patterns were recorded to probe the crystal structure of the as-prepared samples as shown in Fig. 2b. The pristine COF exhibits characteristic diffraction peaks at 3.5° , 5.8° and 26.9° , corresponding to (100), (110) and (001) planes, respectively [46]. The XRD patterns of $\text{MoS}_2@\text{COF}$ composites exclusively possess the diffraction peaks of COF but no obvious peaks belonging to MoS_2 due to the low loading content. It is worth noting that the (100) plane peak intensity of COF gradually decreases with the increase of MoS_2 component. Furthermore, the FT-IR spectrum of COF reveals the obvious appearance of C-N stretching band at 1250 cm^{-1} and the disappearance of N-H stretching band in the 2,6-diaminoanthraquinone, indicating the formation of COF (Fig. S4). The FT-IR spectrum of $\text{MoS}_2@\text{COF}$ agrees well with COF and hardly visible peaks of MoS_2 . Solid-state ^{13}C CP-MAS NMR spectra were collected for the pure COF and $\text{MoS}_2@\text{COF-15}$. Both the COF and $\text{MoS}_2@\text{COF-15}$ exhibit distinctive resonance peaks at 182, 143, and 108 ppm, corresponding to the carbons in C=O, C-N and C=C bonds in the keto-amine form (Fig. S5). The similar spectra reveal that the incorporation of MoS_2 in the synthesis process does not disturb the synthesis and its structure of COF. The actual content of Mo in $\text{MoS}_2@\text{COF-15}$ is 3.84 wt% determined by inductively coupled plasma-mass spectrometry (ICP-MS).

To figure out the electronic interaction between MoS_2 and COF-15, in-situ irradiated X-ray photoelectron spectroscopy (XPS) was carried out for the MoS_2 , COF and $\text{MoS}_2@\text{COF-15}$. The survey scan of the $\text{MoS}_2@\text{COF-15}$ sample in Fig. S6 reveals the coexistence of C, N, O, Mo and S elements, which is in accordance with the EDX results, further verifying the formation of heterojunction materials. As shown in Fig. 3a and b, in comparison with pristine MoS_2 , the XPS binding energy of Mo 3d and S 2p of $\text{MoS}_2@\text{COF-15}$ composite obviously shifts towards lower binding energy in darkness, indicating an increase in the electron

density of MoS_2 . In contrast, compared with the pure COF, the binding energies of O 1s in $\text{MoS}_2@\text{COF-15}$ composite shift to higher energy levels in darkness, implying that the electrons spontaneously transfer from COF to MoS_2 (Fig. 3c). Nevertheless, the C 1s and N 1s XPS binding energy did not exhibit similar phenomena to the O 1s XPS (Fig. 3d and S7). Furthermore, compared with $\text{MoS}_2@\text{COF-15}$ in darkness, the binding energies of Mo 3d and S 2p in $\text{MoS}_2@\text{COF-15}$ composite under light irradiation significantly shift to higher energy levels, while the binding energies of O 1s in $\text{MoS}_2@\text{COF-15}$ composite move to lower energy levels, suggesting the photogenerated electrons transfer from MoS_2 to COF under light irradiation [47,48]. These XPS results suggest the MoS_2 component actually acts as the electron acceptor without illumination but electron donor under illumination in $\text{MoS}_2@\text{COF}$, and provide important evidence for the charge transfer pathway across the heterojunction interface under light irradiation [49].

Density functional theory (DFT) calculations were performed to further reveal the charge transfer in the $\text{MoS}_2@\text{COF-15}$ heterojunction photocatalyst. As shown in Fig. 4a and b, the work functions of MoS_2 and COF were calculated to be about 5.94 and 5.73 eV, respectively, revealing that electrons in COF can transfer to MoS_2 via the heterojunction interface driven by the potential difference until the Fermi energy is equilibrated [50]. This result can be directly proved by charge density difference and planar-averaged electron density difference as illustrated in Fig. 4c and S8. Strikingly, charge redistribution mainly appears near the interface; moreover, the electrons accumulate near the MoS_2 layer, while holes accumulate near the COF layer. The spontaneous charge transfer through the interfacial between MoS_2 and COF is the staple cause for triggering the induced built-in electric field [51]. Combined with in-situ XPS and theoretical calculation results, the charge transfer mechanism of the $\text{MoS}_2@\text{COF-15}$ heterojunction is depicted in Fig. 4d-f. Since the COF has a higher Fermi level than that of MoS_2 , after the contact of MoS_2 and COF in darkness, the electrons of the COF spontaneously flow to MoS_2 until achieving the same Fermi energy level and forming the stable built-in electric field (Fig. 4d). During the process of electron migration, the interface region of COF component is positively charged owing to losing electrons, while the interface region of MoS_2 is negatively charged due to acquiring electrons, giving rise to upward bend of band edge of COF and downward that of MoS_2 (Fig. 4e). Under illumination, both MoS_2 and COF are photoexcited to produce electrons and holes. The built-in electric field enables the transfer of photogenerated electrons accumulated in MoS_2 to COF to recombine with the photogenerated holes (Fig. 4f), revealing that the interfacial charge transfer within the heterojunction possibly conforms to Z-scheme (S-scheme) mechanism [52]. Meanwhile, the photogenerated holes and electrons are maintained on valent band of MoS_2 and the conduction

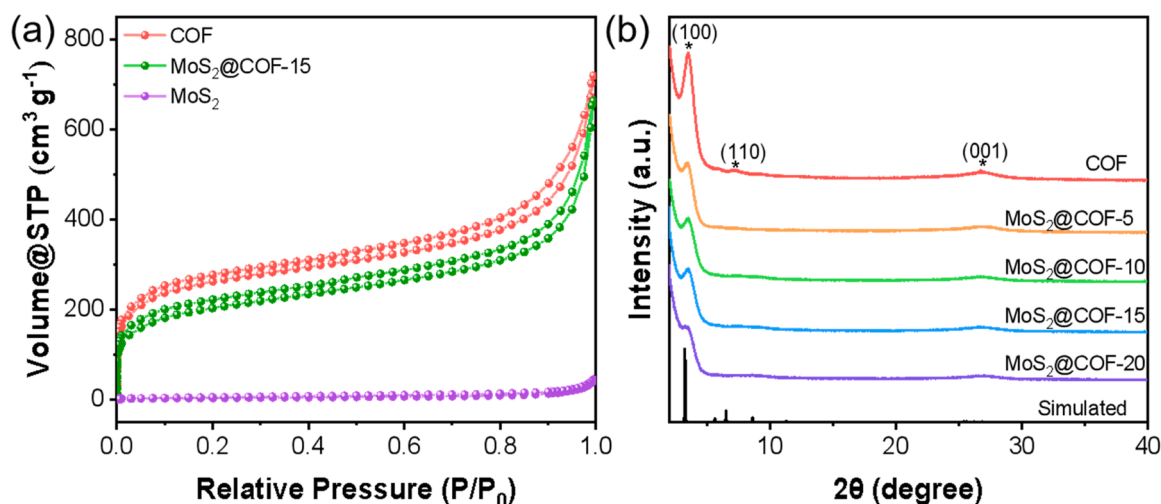


Fig. 2. (a) N_2 adsorption-desorption isotherms of MoS_2 , COF and $\text{MoS}_2@\text{COF-15}$ at 77 K. (b) XRD patterns of COF and $\text{MoS}_2@\text{COFs}$.

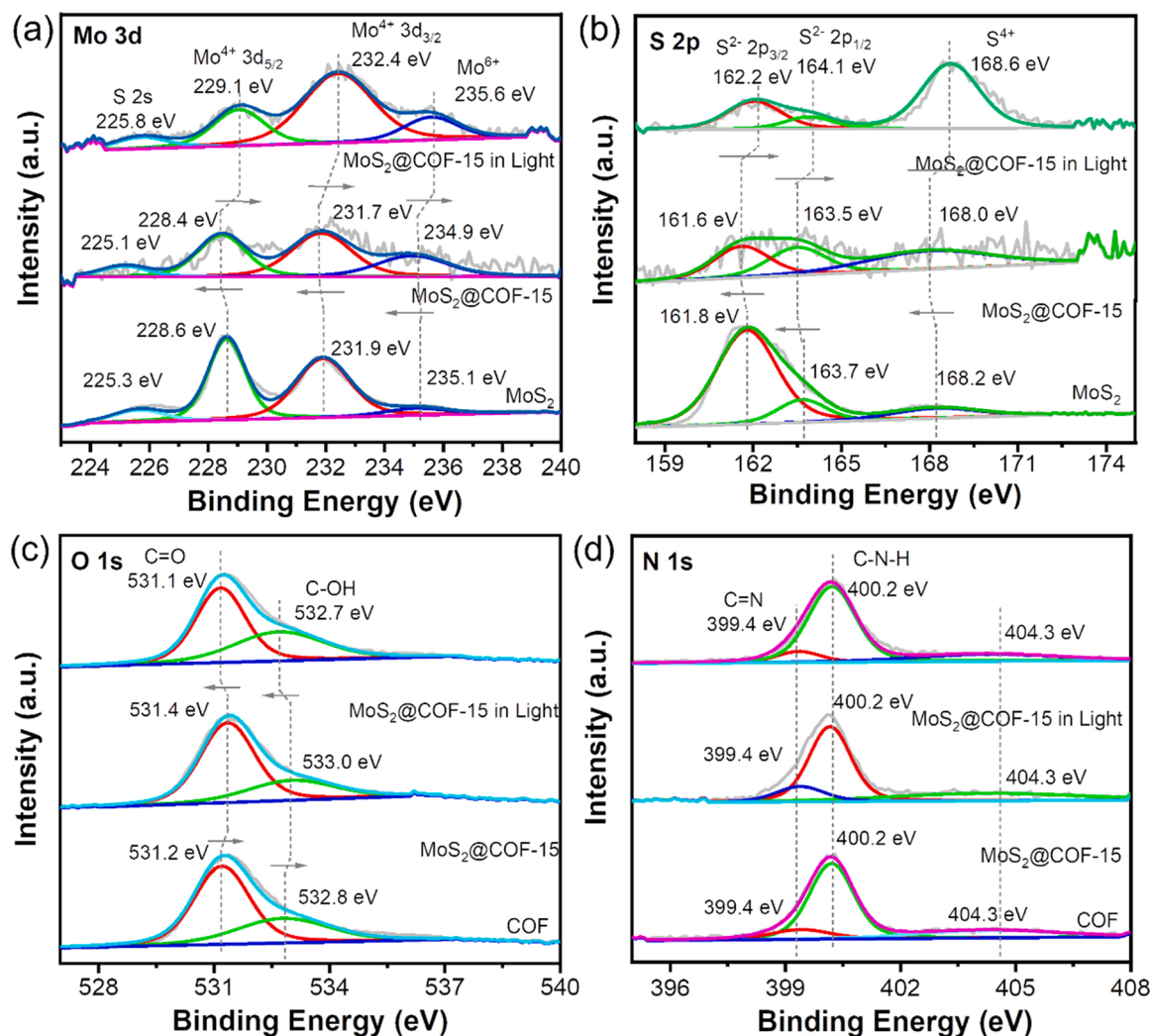


Fig. 3. In-situ XPS spectra of (a) Mo 3d, (b) S 2p, (c) O 1s, and (d) N 1s in pristine MoS₂, COF, and MoS₂@COF-15 samples tested in darkness and under illumination ($\lambda = 300\text{--}2000\text{ nm}$).

band of COF, respectively, which will participate in the photocatalytic CO₂ reaction.

3.2. Optical properties and charge transfer dynamics

The photoelectric properties of MoS₂, COF and MoS₂@COFs were then investigated to assess light absorption, charge separation and surface reactions. The optical absorption behaviors of these samples were first explored by ultraviolet-visible diffuse reflectance spectra (UV-vis DRS). As shown in Fig. 5a, pure COF exhibited strong absorption in visible light region with an absorption edge at 800 nm, while bare MoS₂ presented light absorption in the almost full spectrum owing to its black surface [49]. Compared with pure COF, the light absorption edge of MoS₂@COFs only occurred a slight blue shift, indicating that the great upgrade in the photocatalytic activity of MoS₂@COFs was not ascribed to the change of light absorption. Additionally, the optical bandgap (E_g) of MoS₂, COF and MoS₂@COF-15 were calculated to be about 1.91, 1.69 and 1.87 eV by using Tauc plots analysis, respectively (Fig. S9). Furthermore, Mott-Schottky measurements were performed to determine the conduction band minimum (CBM) potentials of the samples (Fig. S10). The flat band potential (E_b) of MoS₂ and COF was calculated to be -1.11 and -1.44 V (vs. Ag/AgCl, pH = 7), that is, -0.91 and -1.24 V (vs. NHE, pH = 7), respectively. It is known that CBM potential of the n-type semiconductor is typically more negative by approximately

0.1 V than the flat-band potential [53,54]. Therefore, CBM potentials of pure MoS₂ and COF were calculated to be -1.01 and -1.34 V (NHE). The valence band maximum (VBM) positions of pure MoS₂ and COF were situated at 0.90 and 0.53 V, respectively. In this case, the band structures of MoS₂ and COF can be summarized in Fig. S11.

To unveil the photogenerated charge transfer behavior, steady-state photoluminescence (PL) spectra, time-resolved photoluminescence decay (TRPL) spectra and electrochemical measurements were investigated for these samples. As shown in Fig. 5b, the PL intensities of MoS₂@COFs composites were greatly decreased with respect to pure COF, implying that the heterojunction might largely suppress the recombination of photogenerated carriers. Among all of the samples, the MoS₂@COF-15 exhibited the weakest PL intensity, confirming the superior charge separation and migration ability. The average PL lifetime increased from 1.15 ns for COF to 2.46 ns for MoS₂@COF-15 (Fig. 5c), which was mainly attributed to the interfacial charge transfer between MoS₂ and COF in the heterojunction. An improved charge separation efficiency was also confirmed by electrochemical impedance spectra (EIS) and transient photocurrent response. It is noted that the EIS Nyquist plots of the MoS₂@COF-15 possessed a semicircle with the smallest radius than other samples (Fig. 5d), signifying the best charge conductivity and carrier transport capacity [55]. The higher transient photocurrent response of MoS₂@COF-15 further illustrated that constructing a heterostructure is much more conducive to promoting

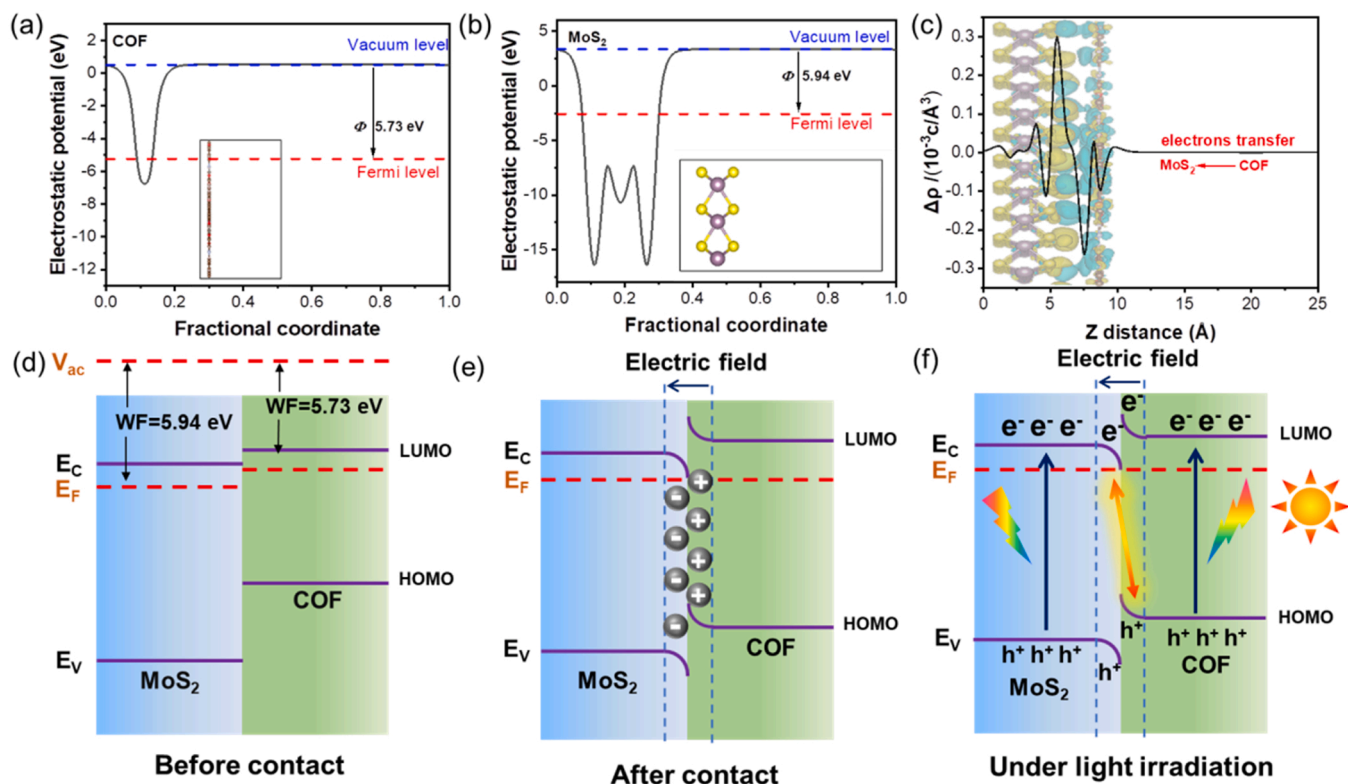


Fig. 4. The calculated work functions of (a) COF and (b) MoS₂. (c) The planar averaged charge density difference $\Delta\rho$ along the Z-direction for the MoS₂@COF-15 (The insert represents the 3D differential charge density map for the MoS₂@COF-15). Schematic illustration of the relative band positions and charge transfer process of COF and MoS₂ (d) before contact, (e) after contact and (f) under light irradiation.

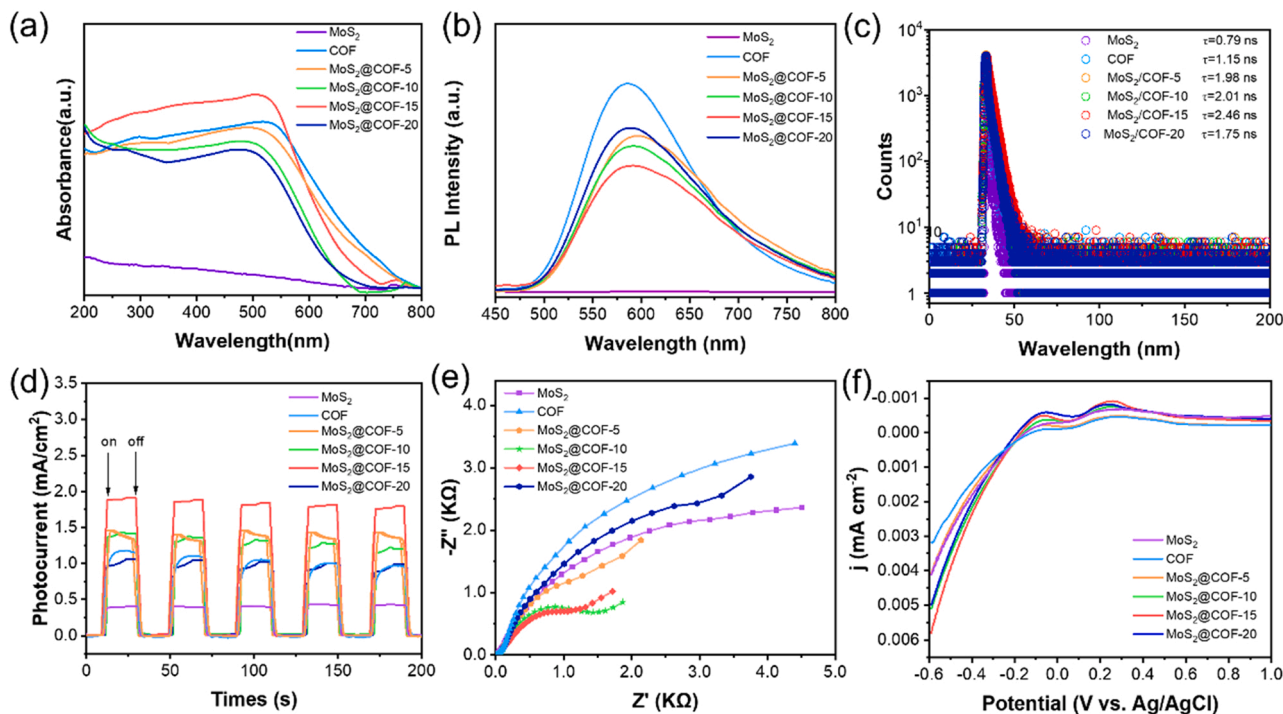


Fig. 5. (a) UV-vis DRS spectra, (b) steady-state PL emission spectra, (c) TRPL spectra, (d) EIS Nyquist plots, (e) I-t curves, and (f) LSV curves in CO₂ atmosphere in darkness and under light illumination of MoS₂, COF and MoS₂@COFs composites.

electron transfer between two semiconducting phases (Fig. 5e). In addition, linear sweep voltammetry (LSV) measurements were also carried out over the MoS₂, COF and MoS₂@COFs composites as

electrodes in the CO₂-saturated KHCO₃ solution (Fig. 5f). After bubbling CO₂ into the electrolyte solution, a higher cathodic current was observed for MoS₂@COF-15 electrode, indicative of the higher CO₂

photoreduction activity of the MoS₂@COF-15 composite [56,57]. By combining these results, it can be reasonably deduced that the heterostructure with strong electron coupling effect dramatically stimulates charge separation and interfacial charge transfer under the action of interfacial electric field.

3.3. Photocatalytic performance CO₂ reduction

The activities of photocatalytic CO₂ reduction performance of as-obtained photocatalysts were evaluated by using [Ru(bpy)₃]Cl₂·6H₂O as photosensitizer and triethanolamine (TEOA) as hole-scavenger in an acetonitrile/water (CH₃CN/H₂O) mixed solution under visible light irradiation. As shown in Fig. 6a and b, the main products were CO, CH₄, and H₂ over the pure MoS₂, achieving generation rates of 80.6, 123.2, and 721.0 μmol·g⁻¹·h⁻¹ respectively; besides, further reduced products C₂+ hydrocarbons, C₂H₄ and C₂H₆ with generation rates being 1.7 and 6.5 μmol·g⁻¹·h⁻¹, were also detected (Figs. S12, S13). No liquid products could be detected from the Nuclear Magnetic Resonance (NMR) spectra after photocatalytic tests (Fig. S14). In contrast, the pure COF presented an inferior activity, but H₂ was not generated, suggesting its high selectivity toward CO₂ reduction. More interestingly, the MoS₂@COF hybrid composites could provide notable selectivity toward C₂H₆ production. In particular, the MoS₂@COF-15 showed the highest rates for C₂H₆ production (56.2 μmol·g⁻¹·h⁻¹), which was 8.6 and 31.2 times higher than those of pure MoS₂ and COF, whereas the generation rates for CO and CH₄ were decreased simultaneously. Meanwhile, the product selectivity of C₂H₆ (83.8%) was also significantly improved, which was more than 27.9 and 7.4 times higher than that for pure MoS₂ and COF, respectively (Fig. 6c). These results indicated that the COF component might have a great contribution to the production of C₂H₆ over the MoS₂@COFs. The enhanced activity and selectivity of MoS₂@COF towards the production of C₂H₆ was possibly ascribed to the increased CO₂ adsorption and higher density of photogenerated electrons, thereby reducing the reaction barrier and stabilizing the CO intermediates moderately. Of note, the photocatalytic performance of MoS₂@COF-15

in C₂H₆ evolution was also competitive compared with previously reported photocatalysts (Table S2). In addition, the mixture of 15% MoS₂ and 85% COF (named as MoS₂+COF) also exhibited a remarkably enhanced C₂H₆ production rate (26.5 μmol·g⁻¹·h⁻¹) compared with the pure samples, but which was obviously lower than that of MoS₂@COF-15. These results testified that the rational construction of MoS₂@COF heterostructures could significantly promote CO₂ conversion to C₂H₆ and suppress competitive hydrogen evolution reaction. Moreover, the apparent quantum yield (AQY) of MoS₂@COF-15 achieved the highest value 0.03% for the photocatalytic CO₂ reduction with monochromatic light at 450 nm (Fig. S15a), which is 7.5 and 2.3 times higher than that of pure MoS₂ and COF (Fig. S15b). The comparative AQY values at the stationary point strongly reveal the superior activity of MoS₂@COF-15, which is believed that the high AQY is ascribed to high charge separation efficiency and carrier mobility in the heterojunction.

Several control experiments were carried out for MoS₂@COF-15 including testing without catalyst, photosensitizer, hole-scavenger, and testing with the catalyst but in the dark or without CO₂ but in Ar under otherwise same reaction conditions. As shown in Fig. 6d, no detectable amount of C₂H₆ was produced in all these cases, indicating their indispensable contributions to the production of C₂H₆. Nevertheless, the production of CO and CH₄ might be observed, especially only with [Ru(bpy)₃]Cl₂ but without catalyst, which suggested that the photosensitizer could act as a catalyst for CO₂ reduction to CO. Furthermore, a small amount of CO and CH₄ product were observed in Ar atmosphere, but their yields were far lower than that under CO₂ atmosphere. The C₁ products could be attributed to residual CO₂ after Ar purging because the CO₂ chemisorbed on the photocatalyst surface was difficult to be completely removed under ambient conditions [58]. Thus, it was not surprising that a small amount of CO and CH₄ could be produced but almost no C₂H₆. Moreover, no any CO₂ products were observed in the darkness. These results unambiguously illustrated that C₂H₆ really originated from the photocatalytic CO₂ reduction reaction rather than carbon contamination [59]. Moreover, the isotope labeling experiment was conducted by using ¹³CO₂ instead of ¹²CO₂ gas to further verify the

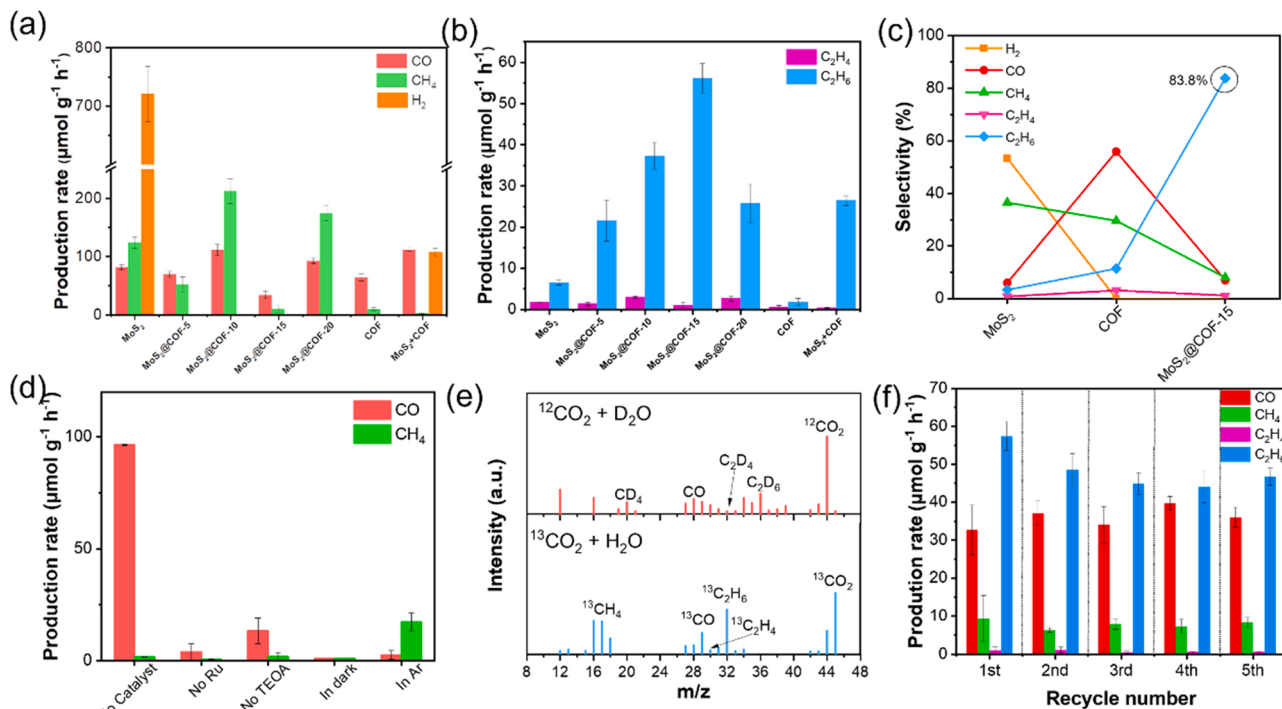


Fig. 6. Photocatalytic CO₂ reduction to (a) C₁ products and (b) C₂ products over as-synthesized photocatalysts. (c) Products selectivity of CO₂ reduction over MoS₂, COF, and MoS₂@COF-15. (d) Control experiments over MoS₂@COF-15. (e) GC-MS analysis for photocatalytic ¹³CO₂ reduction and D₂O over MoS₂@COF-15. (f) Formation rates of CO₂ products in the stability tests of MoS₂@COF-15.

origins of CO_2 reduction products. As shown in Fig. 6e, the corresponding $^{13}\text{CO}_2$ product peak at the peaks at $m/z = 17$, 29 and 32 in the mass spectra might be definitely assigned to $^{13}\text{CH}_4$, ^{13}CO , and $^{13}\text{C}_2\text{H}_6$, respectively, further excluding the possibility of the adsorbed carbonous pollutants on the photocatalyst. Moreover, corresponding CD_4 , C_2D_4 , and C_2D_6 could be detected when using D_2O instead of H_2O , supporting the proton originating from water. The cycling experiments of MoS_2/COF heterojunction catalyst have been conducted and revealed that the formation rates of CO_2 products almost remained unchanged within five consecutive cycles (Fig. 6f). Moreover, FT-IR spectrum and XRD pattern of reused MoS_2/COF exhibited no discernible structural change (Figs. S16 and S17), further implying its great photocatalytic stability.

3.4. Photocatalytic CO_2 reduction mechanism

It is well accepted that CO_2 adsorption and activation on the surface of the catalyst are crucial for photocatalytic CO_2 reduction. Thus, CO_2 adsorption-desorption measurements were performed for MoS_2 , COF

and MoS_2/COF composite to assess their CO_2 adsorption behaviors (Fig. S18). Results indicated that the CO_2 adsorption capacity of the pure COF reached as high as $62.7 \text{ cm}^3 \cdot \text{g}^{-1}$ at 273 K, whereas MoS_2 had almost no CO_2 adsorption capacity in the total pressure due to the lack of porous structure, suggesting that CO_2 molecule was mainly adsorbed on the surface of COF component. The adsorption capacity of MoS_2/COF was slightly lower than that of pristine COF, which is undoubtedly beneficial for subsequent CO_2 activation and reduction process.

To figure out the activation process of photocatalytic CO_2 reduction, the in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on MoS_2/COF composite along with MoS_2 and COF for tracking the evolution of reactive species. Two consecutive procedures namely surface adsorption and photocatalysis process were conducted in darkness and under light irradiation, respectively, as shown in Fig. 7a. After pumping CO_2 and H_2O vapor to saturation in the dark for 30 min, multiple intermediates, including bicarbonate (HCO_3^- , 1419 cm^{-1}) [8], monodentate carbonate (m-CO_3^{2-} , 1555 cm^{-1}), bidentate carbonate (b-CO_3^{2-} , 1294 cm^{-1} , 1508 cm^{-1}) [60], and active $\cdot\text{CO}_2^-$ intermediates (1686 cm^{-1}) [61] were identified on the MoS_2/COF , and

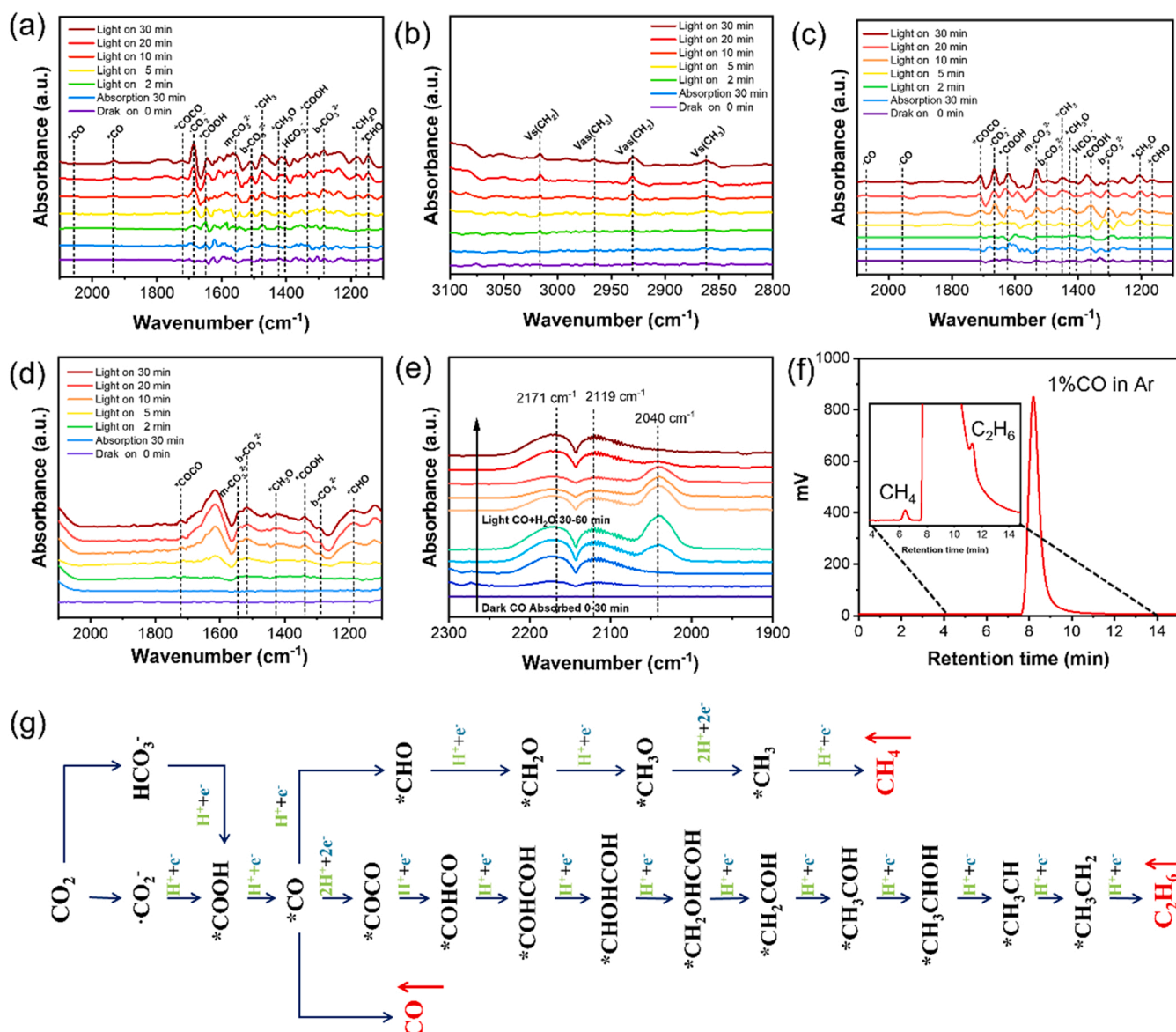


Fig. 7. The in-situ DRIFTS taken during photocatalytic CO_2 reduction of (a, b) MoS_2/COF -15, (c) COF, and (d) MoS_2 . (e) The in-situ CO-DRIFTS of MoS_2/COF -15. (f) GC spectra of photocatalytic CO reduction (1% CO in Ar gas mixture) over MoS_2/COF -15 photocatalyst. (g) Possible reaction pathways for photocatalytic CO_2 reduction. The “*” represents adsorption on the substrate.

suggesting the distinct intermediate bonding interaction of adsorbed CO₂ molecule on the catalyst surface. Upon illumination, it could be observed that the intensity of the absorption peaks generally rises, and several new carbon species, such as formic acid *COOH (1338 cm⁻¹, 1638 cm⁻¹), *CHO (1147 cm⁻¹), *CH₂O (1197 cm⁻¹) and *CH₃O (1436 cm⁻¹) *CO (1935 cm⁻¹, 2056 cm⁻¹), appeared and increased gradually with prolonged adsorption time [11,62,63]. The symmetric stretching vibrations of *CH₂ (3016 cm⁻¹, 2930 cm⁻¹) and *CH₃ (2964 cm⁻¹, 2864 cm⁻¹) were also observed under continuous irradiation in Fig. 7b [64], which were critical intermediates for yielding CH₄. Importantly, the key intermediate of *COCO to obtain C₂ product could be observed at about 1716 cm⁻¹, which provided strong experimental evidence for C-C coupling during the photocatalytic CO₂ reduction. In addition, intermediates HCO₃⁻ (1409 cm⁻¹), m-CO₃²⁻ (1535 cm⁻¹), b-CO₃²⁻ (1301 cm⁻¹, 1504 cm⁻¹), *COOH (1358 cm⁻¹, 1630 cm⁻¹), *CH₃O (1429 cm⁻¹), *CH₂O (1206 cm⁻¹) *CHO (1164 cm⁻¹), and *COCO (1710 cm⁻¹) could also be observed in the spectra of pure COF (Fig. 7c). In contrast, almost no adsorption occurred on the pure MoS₂ in the dark; however, under illumination, partial intermediate species generating CO₂ reduction products were also detected and increased with prolonged adsorption time (Fig. 7d). To exclude the interferences of solvent (CH₃CN), sacrificial agent (TEOA) and photocatalyst, the control experiments of in-situ DRIFTS measurements have been conducted to further verify the origins of CO₂ reduction products (Fig. S19). These results implied that the structure of MoS₂@COF-15 composite was the key role in controlling photocatalytic CO₂ reduction in favor of the C-C coupling pathway to the formation C₂H₆ product.

Combining with these results, a possible pathway of CO, CH₄, and C₂H₆ generation was put forward as shown in Fig. 7g. First, CO₂ molecule was adsorbed and activated into ·CO₂ species, which forms HCO₃⁻, CO₃²⁻, and *COOH intermediates and were subsequently reduced to CO product. Subsequently, it was speculated that the *CO could either be reduced to produce CH₄ or occur dimerization to form *COCO which led to the formation of C₂H₆ with the assistance of the MoS₂ active sites and accelerated electron transfer in the interfaces. To clearly clarify the dimerization of two *CO to produce following C₂H₆, which was our main aim, the in-situ DRIFTS tests were thus carried out by directly employing CO to replace CO₂ to probe into the adsorption behavior of MoS₂@COF-15 towards the *CO. The catalyst was firstly subjected to CO adsorption to saturation and then allowed to desorb in purging H₂O vapor, which reacted with *CO to subsequent hydrogenation. As shown in Fig. 7e, prior to illumination, the peaks at 2171 and 2119 cm⁻¹ could be observed and assigned to free CO molecules adsorbed on the surface [65]. The peak at 2040 cm⁻¹ was attributed to liner CO species adsorbed on the MoS₂@COF-15 photocatalyst and increased gradually with prolonged time in darkness, indicating stronger chemical interactions with *CO in the heterojunction. However, it was difficult to determine where CO was adsorbed on either MoS₂ or COF. Meanwhile, it was noted that when charging H₂O vapor under light illumination, the CO species at 2040 cm⁻¹ were consumed gradually until disappeared, suggesting that the *CO was subsequently reduced to form CH₄ and C₂H₆ products. To further verify this conclusion, we performed the CO reduction by using the low concentration CO (1% CO in Ar gas mixtures) instead of CO₂ in the MoS₂@COF-15 photocatalyst under otherwise identical conditions, and as expected, CH₄ and C₂H₆ products still were detected by gas chromatography (Fig. 7f). Moreover, additional in-situ DRIFTS tests were also conducted by purging N₂ to desorb adsorbed CO from the catalyst. As shown in Fig. S20, the peak at 2040 cm⁻¹ in CO-DRIFTS retained half intensity after N₂ purging, whereas the free CO molecule disappeared, indicating that MoS₂ had a higher CO chemisorbed affinity due to higher electron density while COF mainly presented physical absorption [66]. It was thus proved that the catalyst structure was crucial for controlling the product distribution of CO₂ reduction.

To further reveal the mechanism of CO₂-to-C₂H₆ conversion, DFT calculations were performed on the COF and MoS₂ components of MoS₂@COF-15, respectively. The Gibbs free energy profiles of *CO₂-to-

*CO reduction, *CO-to-*COCO dimerization, and *C₂H₆ formation were depicted in Fig. 8a. The calculation results suggested that the formations of *COOH and *COCO were the main rate-limiting steps for both components. The COF component had a much lower kinetic energy barrier (0.54 eV) for *CO₂ hydrogenation to *COOH compared to that on MoS₂ (2.10 eV), proving that the formation of *COOH mainly occurred on the COF. The production of the *CO intermediate was exothermic, and *CO was easier to adsorb on the MoS₂ component with higher desorption energy. It has been previously demonstrated experimentally and computationally that the generation of C₂₊ products was determined by the energy barriers of generating *COCO via C-C coupling of *CO. The process of *CO dimerization to *COCO on MoS₂ required a much higher energy input (1.53 eV) compared with that on COF (0.19 eV), which indicated that it was easier to generate *COCO at COF. Moreover, *CO tended to generate of *COCO instead of desorbing *CO to CO gas, revealing that the heterojunction played a decisive role in C-C coupling. Given that the hydrogen evolution reaction is a thermodynamic competitive process of CO₂ reduction, the Gibbs free energy of *H formation was also calculated. The formation of *H on COF required a lower energy barrier (0.52 eV) than that on MoS₂ (1.97 eV), indicating its better suppression (Fig. 8b). These results suggest that the whole process more tends to occur in COF component of MoS₂@COF heterojunction with the assistance of MoS₂ in thermodynamics.

Furthermore, during photocatalysis, an electron transfer process from [Ru(bpy)₃]Cl₂ to catalyst might be involved by their matched energy levels (Fig. S21). To verify this point, the photoluminescence quenching experiments by adding different amounts of MoS₂@COF-15 to a CH₃CN aqueous solution of [Ru(bpy)₃]Cl₂ and TEOA were conducted (Fig. 8c), and the intensity of emission peak of [Ru(bpy)₃]Cl₂ was continuously quenched with an increasing amount of MoS₂@COF-15, indicating that the recombination of photogenerated electron and holes had been substantially suppressed, in other words, the occurrence of electron transfer from the excited [Ru(bpy)₃]Cl₂ to MoS₂@COF-15. Moreover, the fitting of time-resolved luminescence decay profile of [Ru(bpy)₃]Cl₂ exhibits a long lifetime of 209.4 ns. When 1.0 mg MoS₂@COF-15 was introduced, the photoluminescence of [Ru(bpy)₃]Cl₂ was immediately quenched and the average lifetime reduced to 82.1 ns (Fig. S22). These results strongly suggested that the integration of MoS₂@COF-15 with photosensitizer was beneficial for charge transfer to trigger this photocatalysis. Finally, the possible mechanism for CO₂ photoreduction over MoS₂@COF-15 is proposed and presented in Fig. 8d. Under light illumination, the photosensitizer [Ru(bpy)₃]²⁺ is excited to the excited state, which is capable of donating electrons along with transferring to arrive at the surface of MoS₂@COF-15 and forms [Ru(bpy)₃]³⁺ [67]. The [Ru(bpy)₃]³⁺ is then reductively quenched by sacrificial electron donor TEOA to initial state [Ru(bpy)₃]²⁺ to complete the entire cycle by providing electron. The electrons in the CB of MoS₂ migrate to the HOMO of COF and partially combine with the photoexcited holes, then are further excited to the LUMO of COF. As a result, the electrons accumulated in the LUMO of COF with stronger reducibility to reduce CO₂, while others participate in the H₂ evolution reaction. Meanwhile, the generated CO is released as free CO₂ product and partially adsorbed CO molecules are further hydrogenated with the electrons accumulated in the LUMO of COF to form CH₄ or go through the C-C coupling pathway to form C₂H₆ with the assistance of reversible redox process of anthraquinone in the COF [68,69]. The anthraquinone-based reversible redox reaction is believed to be favorable to speed up electron migration and promote continuous hydrogenation of *CO, thereby significantly enhancing photocatalytic activity and selectivity.

4. Conclusions

In summary, we have constructed the covalently integrated MoS₂@COF hybrid composites via a multistep synthesis route, in which amino-modified MoS₂ was wrapped by anthraquinone-based COF and

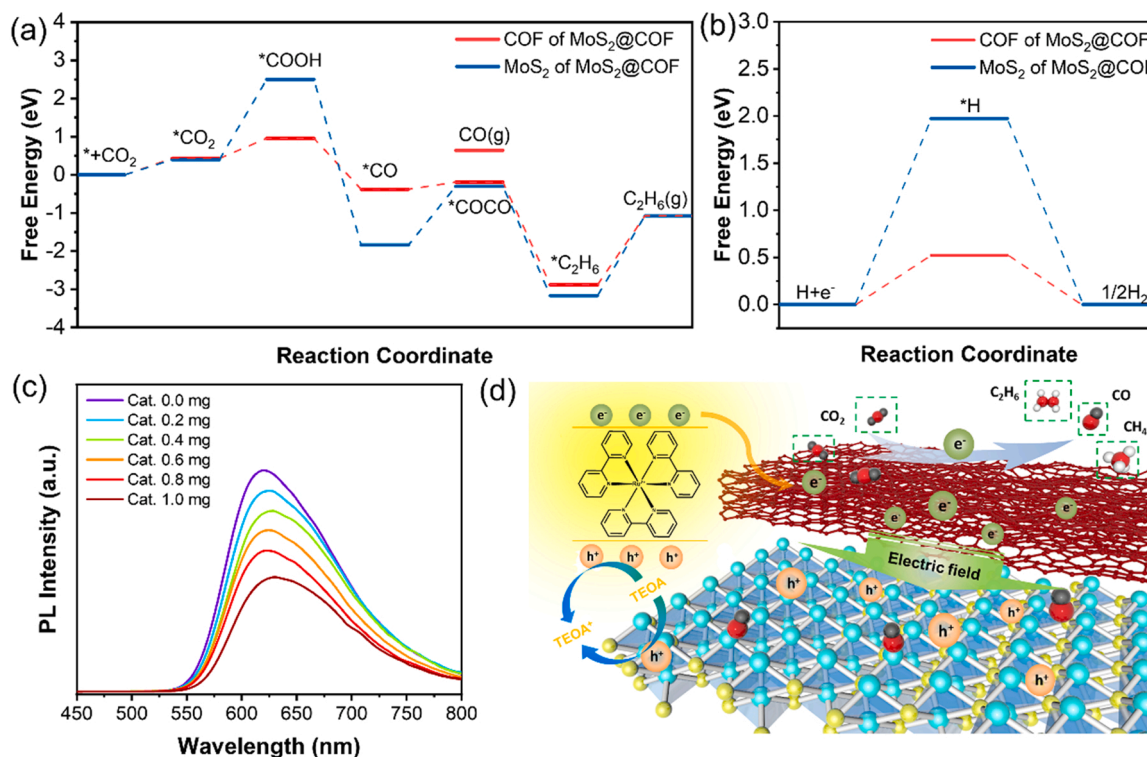


Fig. 8. Gibbs free energy profiles of photocatalytic CO₂ reduction (a) and hydrogen evolution reaction (b) on COF and MoS₂ component of MoS₂@COF-15. (c) Steady-state fluorescence spectra of [Ru(bpy)₃]Cl₂ upon the addition of MoS₂@COF-15 (λ_{ex} = 420 nm). (d) Possible mechanism for the CO₂ reduction by MoS₂@COF composites.

directed its growth along with amino groups. Experimental observations and DFT calculations demonstrate that the interfacial electric field built in the heterojunction accelerates the photogenerated electrons transfer from MoS₂ to COF under light irradiation, resulting in facilitated charge separation and transfer, and thus effectively promoting the activity and C₂H₆ selectivity for photocatalytic CO₂ reduction. Remarkably, the optimized MoS₂@COF-15 achieves C₂H₆ production rate up to 56.2 μmol·g⁻¹·h⁻¹ with 83.8% of selectivity, which is 8.6 and 31.2 times higher than that of pure MoS₂ and COF, respectively. The in-situ DRIFTS and DFT calculations indicate that the structure of MoS₂@COF composite benefits the adsorbed CO₂ activation and promotes adsorbed CO to convert into C₂H₆ product by subsequent hydrogenation and C-C coupling pathway. This work provides new insight into the rational design of photocatalysts for the controllable production of C₂+ hydrocarbons.

Supporting information

Supplementary experimental procedures, characterizations including FT-IR spectra and PXRD patterns of pristine MoS₂, FT-IR spectra, pore size distributions, XPS spectra, Tauc plots, Mott-Schottky plots, experimental estimated band structure diagrams, CO₂ adsorption-desorption curves, in-situ DRIFTS of as-synthesized MoS₂, COF and MoS₂@COF-15, differential charge density map of MoS₂@COF-15. GC and NMR chromatograms of product sample. FT-IR spectra and XRD patterns of reused and fresh MoS₂@COF-15.

Author contributions

The manuscript was written through contributions of all the authors. All authors have given approval to the final version of the manuscript.

CRediT authorship contribution statement

Xianheng Yang : Investigation, Formal analysis, Data curation. **Xingwang Lan**: Methodology, Visualization, Formal analysis, Calculation, Writing – original draft, Project administration. **Yize Zhang**: Investigation. **Hangshuai Li**: Investigation. **Guoyi Bai**: Resources, Supervision, Project administration,

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21908038, 22078080), Science and Technology Project of Hebei Education Department (BJK2022045), Interdisciplinary Research Program of Natural Science of Hebei University (DXK202114). The authors also acknowledge the High-Performance Computing Center of Hebei University.

Notes

The authors declare no competing financial interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the

online version at doi:10.1016/j.apcatb.2023.122393.

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